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Comparison of the biocidal efficiency of alternative disinfectants

John C. Hoff and Edwin E. Geldreich

Of all the current potential alternatives to free residual chlorine for drinking water disinfection (ozone, chlorine dioxide, and chloramines), ozone is the most potent biocide. Chlorine dioxide is about on a par with hypochlorous acid, but in contrast to free residual chlorine, its efficiency increases substantially as pH increases in the range at which disinfection is usually applied. Chloramines are weaker biocides than hypochlorite ion, the least efficient form of free residual chlorine. Precise quantitative ranking of biocidal efficiencies is not possible because efficiencies differ with different microorganisms and experimental conditions. Laboratory studies are not always directly applicable to disinfectant use in the field.

Disinfectants are primarily used in the drinking water treatment process to ensure the destruction of pathogenic microorganisms, thereby preventing the transmission of disease by drinking water. The presence of a disinfectant residual in the distribution system also helps to maintain water quality by preventing the growth of nuisance microorganisms. Many chemical and physical agents have been studied with regard to their potential as drinking water disinfectants. Of these, only ozone, chlorine dioxide, and chloramines are currently considered to be immediately viable alternatives to free residual chlorine for use as primary disinfectants. This group of disinfectants are considered here with regard to their biocidal capabilities.

Disinfection: a kinetic process

Biocidal activity by chemical disinfectants is frequently considered as being

TABLE 1
*Comparison of virus inactivation by free residual chlorine at pH 6.0 and 10.0, and 5.0°C ± 0.2°C**

Virus Strain	Time Elapsed for 99 Percent Inactivation—*min*		
	pH 6.0	pH 10.0	Ratio†
Coxsackie A9 (Griggs)	0.3	1.5	5
Echo 1 (Farouk)	0.5	96.0	192
Polio 2 (Lansing)	1.2	64.0	53
Echo 5 (Noyce)	1.3	27.0	21
Polio 1 (Mahoney)	2.1	21.0	10
Coxsackie B5 (Faulkner)	3.4	66.0	19

*After Engelbrecht et al[4]
†Time required at pH 10.0/Time required at pH 6.0

TABLE 2
Summary of disinfectant characteristics relating to biocidal efficiency

Disinfectant	Rating*		pH Effects on Efficiency (pH Range 6–9)
	Biocidal Efficiency	Stability	
Ozone	1	4	little effect
Chlorine dioxide†	2	2	pH increase is beneficial
Free chlorine†	3	3	pH increase is detrimental
Chloramines	4	1	little effect

*1 = best, 4 = worst
†Ranking influenced by pH

analogous to a chemical reaction, with the microorganism and the disinfectant serving as the reactants. In considering the effectiveness or efficiency of biocidal agents, the rate at which the reaction or destruction of the microorganism population proceeds is the measure used for comparison. The comparative biocidal efficiency of disinfectants is frequently expressed as the relative concentration (e.g., mg/L) of different disinfectants needed to obtain equivalent disinfection rates or as the relative inactivation rates produced by the same concentration of different disinfecting agents. Most of this information has been obtained by laboratory experimentation under carefully controlled conditions in "clean" systems free of extraneous disinfectant-demanding substances, using pure cultures of the microorganism under study.

Determination of comparative efficiency

An example of a typical curve from such an experiment is shown in Figure 1. Percent survival of the microorganism is plotted logarithmically versus time. The horizontal and vertical lines drawn in Figure 1 illustrate the method used for selecting data points to be used in determining comparative efficiency. Data from the results of a number of such experiments, conducted using different disinfectants at various concentrations while maintaining other conditions constant, can be used to construct logarithmic plots of the type shown in Figure 2. As indicated, these results show the times and concentrations of several disinfectants needed to produce a given level of inactivation (e.g., 99 percent) of a test microorganism—in this case, *Escherichia coli*. This figure is a composite of results obtained in one laboratory[1,2] over a period of years, using consistent experimental methods and microorganisms. The results show that ClO_2 at pH 7 and HOCl at pH 6 produce similar rates of inactivation of *E. coli*. Hypochlorite ion (OCl^-) at pH 10 was less effective, and chloramines were even less effective than OCl^-. From the data shown in this figure, the degree of difference in efficiency between the disinfectants could be calculated and expressed quantitatively. For example, HOCl inactivated *E. coli* 35 times as rapidly as did OCl^-.

A similar plot showing virucidal efficiency of these disinfectants for poliovirus 1 is shown in Figure 3. In general, higher disinfectant concentrations and longer contact times were needed for inactivation of poliovirus 1 than for *E. coli*. The differences are on the order of < 1 to 2 orders of magnitude, depending on the disinfectants compared. Also, the difference in efficiency between HOCl and OCl^- was only about fourfold; the efficiency order of the chloramines was reversed.

Studies from which similar curves can be prepared have not been done using ozone as the disinfectant, largely because ozone is such a powerful and unstable disinfectant that limitations on sampling times and ozone measurements make it difficult to obtain good experimental results. The following data illustrate the high rate at which ozone inactivates microorganisms. Sproul et al[3] showed that > 99.999 percent reduction of *E. coli* occurred in 10 s at an initial ozone concentration of 0.38 mg/L. Similarly, 99.7 percent reduction of poliovirus 1 occurred in 10 s at an initial ozone concentration as low as 0.012 mg/L.

Factors affecting comparative disinfection efficiency

Microorganism effects. As shown in Figures 2 and 3, neither order of efficiency nor the degree of difference between the disinfectants was the same for *E. coli* as for poliovirus 1. Further evidence of such differences is shown in Table 1. In this study[4] the rate of inactivation of six different enteroviruses by HOCl and OCl^- was examined. The data shown were collected under carefully controlled experimental conditions in the absence of extraneous disinfectant demand. Each of the results shown represents an average value based on three or more experiments. The results indicate that the degree of difference in disinfection efficiency of HOCl and OCl^- ranged from fivefold for Coxsackie A9 virus to 192-fold for Echo 1 virus. Differences were observed in the rates of inactivation of different viruses by HOCl (10-fold) and OCl^- (60-fold).

pH effects. The pH of the water being disinfected is also an important factor relating to the efficiency of some disinfectants, notably free chlorine and chlorine dioxide. In the case of chlorine, disinfection efficiency declines rapidly as the pH is increased from 7 to 9. This results from the change in disinfectant species present from predominantly HOCl at pH 7 to predominantly OCl^- at pH 9. The efficiency of chlorine dioxide also changes substantially over this pH range, but in contrast its efficiency increases as pH increases (Figure 4).[2] In this case, the change appears to be a function of microorganism sensitivity rather than one of change in disinfectant species present, since chlorine dioxide does not dissociate or disproportionate into different chemical species within this pH range. In earlier studies a similar effect was shown with *E. coli*, i.e., more rapid inactivation by equivalent levels of ClO_2 at pH 8.5 than at lower pHs.[5]

Dissolved salt effects. In 1972 Scarpino et al[6] reported that OCl^- was a more efficient virucide than HOCl against poliovirus 1. Results of subsequent unpublished studies indicated that 0.05 M KCl present in the buffer used in the OCl^- experiments was responsible for the increased virucidal efficiency of OCl^-. Additional studies by Engelbrecht et al[4] confirmed and extended the earlier studies and showed that 0.05 M KCl enhanced the virucidal efficiency of both OCl^- and HOCl (Figures 5 and 6). Others have also confirmed this effect and shown that similar effects are produced by the presence of NaCl and $CaCl_2$.[7-9] This effect was not seen in *E. coli* disinfection studies reported by Scarpino et al[6] although the same KCl-containing buffer was used in the *E. coli* studies.

From the information provided above, it is evident that it is not possible to rank these disinfectants precisely and quantitatively as to their biocidal efficiency. Two primary reasons for this are that different microorganisms react differently and that the same microorganism may react differently under various experimental conditions. It is important to note that the effects described above reflect differences in inactivation rates; that is, the question is not whether inactivation occurs, but at what rate it occurs.

Application of laboratory study results to field situations

While information derived from laboratory studies is useful in assessing the biocidal efficiency of disinfectants, other factors enter into the picture when this information is applied to actual drinking water treatment. Under field conditions the water being treated does not contain clean suspensions of pure cultures of organisms. The medium is not free of extraneous materials that might react with the disinfectant used. Field conditions are such that the biocidal capability of a disinfectant can be altered or even destroyed. A variety of microorganisms are present in their "natural" state, suspended in a medium that contains a variety of other solid and dissolved materials, some of which can have pronounced effects on disinfectant concentration and activity. Because of these effects, it can be assumed that disinfection does not operate as a constant-rate process in the field as it does in laboratory studies. However, some of these conditions can be simulated in laboratory experiments and thus provide information that will have more relevance to actual practice.

It has long been considered that microorganisms' association with particulate matter could result in their being shielded from disinfectant action. This has been the major consideration in establishing a turbidity limit for drinking water. Until recently little direct evidence of such protective effects has been available. The results of some of these recent studies[10] are shown in Figures 7 and 8. Figure 7 shows that poliovirus association with washed cell debris offers substantial protection against inactivation by HOCl to the associated virus in comparison to a freely suspended virus. Similarly, Figure 8 shows that coliforms associated with washed primary effluent solids are inactivated by HOCl much more slowly than clean suspensions of laboratory-grown *E. coli*.

Hijkal et al[11] also have shown that poliovirus associated with fecal material is provided substantial protection against inactivation by chlorine. Sproul et al[3] showed that cell debris-associated virus was also protected from inactivation by ozone, the most efficient biocide

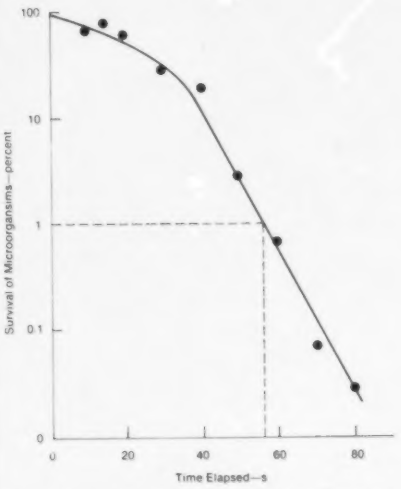

Figure 1. Inactivation of *E. coli* at 15° C at pH 7.0 by 0.16 mg/L chlorine dioxide
After Scarpino et al[2]

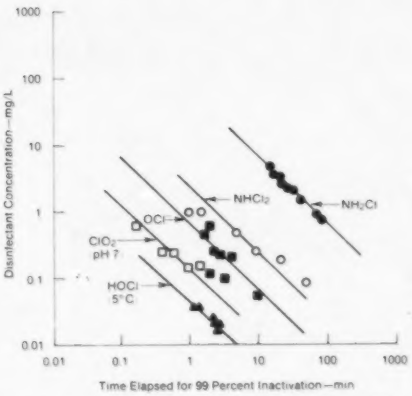

Figure 2. Inactivation of *E. coli* (ATCC 11229) by free and combined chlorine species and chlorine dioxide at 15°
After Esposito[1] and Scarpino et al[2]

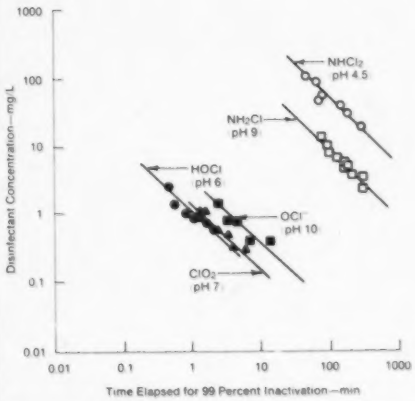

Figure 3. Inactivation of poliovirus 1 by free and combined chlorine species and chlorine dioxide at 15° C
After Esposito[1] and Scarpino et al[2]

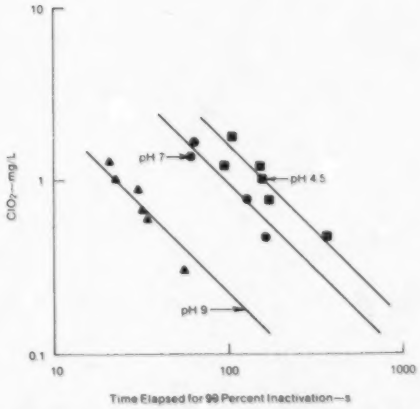

Figure 4. Effect of pH on inactivation of poliovirus 1 (Mahoney) by chlorine dioxide at 21° C
After Scarpino et al[2]

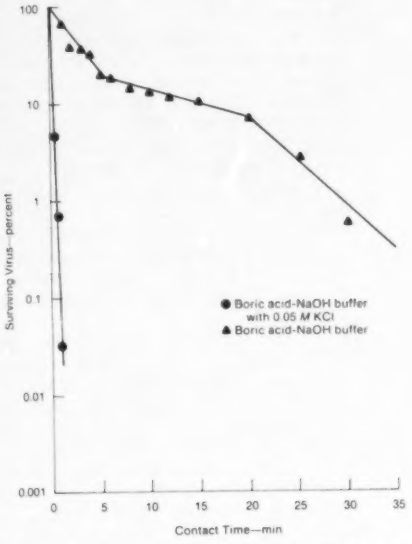

Figure 5. Inactivation kinetics of poliovirus 1 by 0.46–0.49 mg/L free available chlorine in 0.05 *M* boric acid-NaOH buffer, with and without 0.05 *M* KCl at pH 10.0 and 5.0° C
After Engelbrecht et al[4]

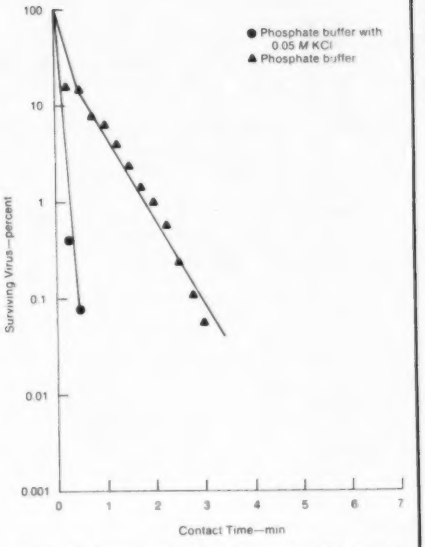

Figure 6. Inactivation kinetics of poliovirus 1 by 0.48–0.49 mg/L free available chlorine in 0.05 *M* phosphate buffer, with and without 0.05 *M* KCl at pH 6.0 and 5.0° C
After Engelbrecht et al[4]

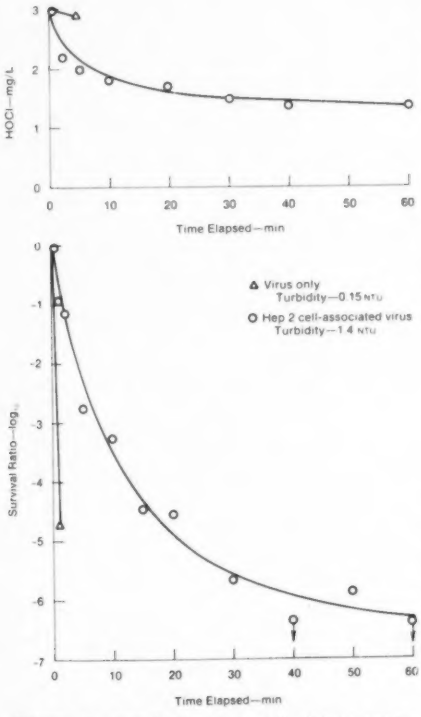

Figure 7. Inactivation of cell debris-associated poliovirus by free chlorine at pH 6.0 and 5° C
After Hoff[10]

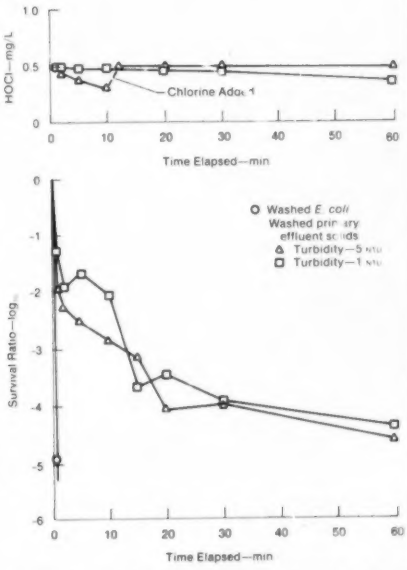

Figure 8. Inactivation of coliforms associated with primary effluent solids at pH 6.0 and 5° C
After Hoff[10]

under consideration. Ozone levels in excess of 2 mg/L failed to completely inactivate viruses associated with cell debris in 30 s. In longer-term experiments, viruses could be detected even after exposure for 75 min to an initial ozone level of 2.5 mg/L. Comparable information for chlorine dioxide and chloramines is not yet available, but in view of the ozone results it appears likely that they will show the same limitations in efficiency for inactivating cell debris-associated microorganisms.

Adequacy of chlorammoniation for primary disinfection

For many utilities conversion to the use of chloramines rather than free residual chlorine provides the simplest solution to the trihalomethane problem. Despite the poor biocidal efficiency of chloramines, there is evidence that the chlorammoniation process has been used successfully for years by a number of utilities. It is important to note that the way chloramines are formed and used in the field differs from the procedures used in the laboratory experiments described above.

In the experimental work, the chloramines were preformed and the microorganisms were added subsequently. In conventional chlorammoniation as practiced in the field, ammonia is added to the water first. Chlorine addition then follows, usually in the form of chlorine gas. The rate of conversion of free chlorine to chloramines is dependent on pH, temperature, and the ratio of chlorine to ammonia present. While the reaction occurs in hundredths of a second at higher temperatures and optimum pH (8.3), it can occur at much slower rates at lower temperatures and lower or higher pHs. Therefore, the presence of free chlorine for several minutes could result in rapid inactivation of microorganisms, particularly at lower pH levels, because free residual chlorine is present in the form of HOCl.

This was suggested by Hoather[12] and Houghton[13] as an explanation for the much faster bactericidal action observed in ammonia-chlorine treatment than could be shown using preformed chloramines. In more recent pilot-scale chlorammoniation studies involving both clean water and tertiary effluent, Selleck et al[14] ascribed the initial rapid phase of bactericidal action during chlorammoniation to oxidation-reduction reactions occurring between the chlorine and substances present in the water rather than to unreacted free chlorine. They postulated that highly reactive, short-lived free radicals produced during the oxidation of ammonia nitrogen may be responsible for the rapid inactivation of bacteria.

From these studies it appears that the much slower inactivation rates shown by

preformed chloramines may not be directly relevant to chlorammoniation in the field. However, it also should be pointed out that the enteroviruses are much more resistant than coliforms to both free residual chlorine and chloramines. Whether or not the initial rapid inactivation phase would be of sufficient duration to ensure virus destruction would depend on the source water and other treatment processes used. Because of this, it would seem that conversion from free chlorine to chlorammoniation for primary disinfection should be considered with caution. In fact, Selleck et al[14] stated that the existing data on this phenomenon are much too fragmentary to permit the analysis of all situations.

Conclusions

Some of the characteristics relating to the biocidal efficiency of the four disinfectants under consideration are summarized in Table 2. It is clear that none of the disinfectants is optimal in all respects. When it is necessary to consider alternatives to chlorine, biocidal efficiency is a primary factor. However, many other factors must also be weighed. Preliminary consideration has been given to disinfecting agents other than chlorine and it is possible that future studies will result in more effective disinfectants or combinations of disinfectants for drinking water treatment.

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